

⑩



Eur päisches Patentamt

Eur pean Patent Office

Office européen des brevets

⑪ Publication number:

**0 175 578**  
**B1**

⑫

## EUROPEAN PATENT SPECIFICATION

⑬ Date of publication of patent specification: 27.12.90

⑭ Int. Cl.<sup>6</sup>: G 21 K 4/00

⑮ Application number: 85306650.4

⑯ Date of filing: 18.09.85

⑰ Radiographic image storage panel and its preparing process.

⑱ Priority: 18.09.84 JP 196365/84

⑲ Date of publication of application:  
26.03.86 Bulletin 86/13

⑳ Publication of the grant of the patent:  
27.12.90 Bulletin 90/52

㉑ Designated Contracting States:  
DE NL

㉒ References cited:  
EP-A-0 100 483  
EP-A-0 102 790  
GB-A-2 096 160

㉓ Proprietor: KONICA CORPORATION  
26-2, Nishi-shinjuku 1-chome Shinjuku-ku  
Tokyo (JP)

㉔ Inventor: Tsuchino, Hisanori  
6-5-2 Tamadaira  
Hino-shi Tokyo (JP)  
Inventor: Kano, Akiko  
2-19-8 Owada-machi  
Hachioji-shi Tokyo (JP)  
Inventor: Amitani, Koji  
1-8-14 Tamadaira  
Hino-shi Tokyo (JP)  
Inventor: Shimada, Fumio  
3-5-20 Kawasaki Hamura-machi  
Nishitama-gun Tokyo (JP)

㉕ Representative: Ellis-Jones, Patrick George  
Armine et al  
J.A. KEMP & CO. 14 South Square Gray's Inn  
London WC1R 5EU (GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

**EP 0 175 578 B1**

## Description

## Background of the invention

This invention relates to a radiographic image storage panel, and especially to a radiographic image storage panel which provides a radiographic image having high sharpness.

A radiographic image such as an X-ray image has been widely used for diagnosis of diseases and the like. For the purpose of obtaining such an X-ray image, an X-ray radiophotographic method wherein a phosphor layer (a fluorescent screen) is irradiated with X-rays which are transmitted by a subject to produce visible rays and a silver salt-coated photographic film is irradiated with said visible rays and then developed in the usual photographic manner, is applied. In recent years, however, methods to obtain a photographic image directly from the fluorescent screen without using a silver salt-coated film have been developed.

As such a method, there may be cited, for example, a method wherein first, radioactive rays which are transmitted by a subject are absorbed by a fluorescent screen, then said screen is excited by light or thermal energy or the like so that said screen may emit fluorescence radiation energy which is absorbed and accumulated, and then said emitted fluorescence is detected to make an image. For example, methods of radiographic image storage to use a stimutable phosphor and to use visible or infrared rays as stimutable excitation rays have been proposed by U.S. Patent No. 3,859,527 and Japanese Patent O.P.I. Publication No. 12144/1980. In radiographic image storage using these methods, the layer containing a stimutable phosphor is formed on a support. This layer is irradiated with radioactive rays which are transmitted by the subject to accumulate radiation energy in accordance with the transmission rate of every site of the subject so as to build a latent image, and this is then scanned with stimutable excitation rays to make the accumulated radiation energy emit at every site. The emitted radiation energy is converted to light, and then the image is made according to optical signals based on the variation of intensity of the light. This final image can either be regenerated as a hard copy, or regenerated on CRT.

For the radiographic image storage panel, which has a layer containing a stimutable phosphor, it is necessary that not only both the absorption rate of radiation and conversion rate to light (hereinafter both together are referred to as "radiosensitivity") are high, but also that the final image possesses good graininess and sharpness, similar to the case of the afore-mentioned radiography using fluorescent screen.

However, since such a radiographic image storage panel, which has a layer containing a stimutable phosphor, is in general prepared by coating a dispersion which contains both stimutable phosphor particles with particle sizes ranging from 1  $\mu\text{m}$  to 30  $\mu\text{m}$  or so, and some organic binder, on its support or protective layer, the packing density of the stimutable phosphor is necessarily as low as 50%, and consequently the layer containing the stimutable phosphor has to be thicker to secure a sufficiently high radio-sensitivity as shown in Fig. 3. While the quantity of the stimutable phosphor adhered is about 50 mg/cm<sup>2</sup> when the thickness of the layer is about 200  $\mu\text{m}$ , the radiosensitivity linearly rises until the thickness reaches about 350  $\mu\text{m}$ , but levels off over about 450  $\mu\text{m}$  thickness. Such a levelling-off of the radiosensitivity is caused because some of the emission of the stimutable fluorescence from the inside the layer containing the stimutable phosphor is dispersed among the stimutable phosphor particles.

On the other hand, in the above radiographic image storage methods, the thinner the layer containing the stimutable phosphor is, the sharper the obtained image tends to be as shown in Fig. 4; therefore, it is necessary to make said layer as thin as possible to improve the image sharpness.

In addition, since the image graininess according to the above radiographic image storage methods definitely depends on the locational fluctuations of a number of radiation quanta (quantum mottles), and/or structural disturbances of the layer containing the stimutable phosphor of the radiographic image storage panel (structure mottles), reducing the thickness of said layer causes an increase in quantum mottles through a decrease in the number of radioactive quanta absorbed in said layer, and/or a decrease in structure mottles through the actualization of structural disturbances, resulting in a deterioration of the image quality. Therefore, it is necessary to make said layer as thick as possible to improve the image graininess.

Thus, so far as the thickness of the layer containing a stimutable phosphor in such a conventional radiographic image storage panel is concerned the radiosensitivity or graininess of the resulting image, and the sharpness of the image pose quite opposite requirements; therefore such panels have necessarily been made as a compromise between different requirements of both the radiosensitivity or graininess, and the sharpness.

As is well known, the image sharpness in conventional radiography depends on the diffusion of the instantaneous fluorescence (the fluorescence on irradiating) of the phosphor in the fluorescent screen, whereas the image sharpness in the above radiographic image storage method using stimutable phosphor does not depend on the diffusion of the stimutable fluorescence by the stimutable phosphor in the radiographic image storage panel, but depends on the extension of the stimutable excitation rays in said panel. The reason for this is as follows. In such a radiographic image storage method, the radiographic image information accumulated in the panel is read on a time series basis, i.e. the stimutable fluorescence produced by excitation rays irradiated at a certain time ( $t_1$ ) is recorded as the output from a certain pixel ( $x_1, y_1$ ) on the said panel. If the said excitation rays extend through the said panel due to dispersion or the like, and excite stimutable phosphor particles outside the pixel ( $x_1, y_1$ ) actually irradiated, the output from the

## EP 0 175 578 B1

area wider than said pixel ( $x_i, y_i$ ) would be recorded as the output from said pixel. However, if the stimuable fluorescence by the excitation rays irradiated at the time ( $t_i$ ) is the only fluorescence from said pixel ( $x_i, y_i$ ) on the panel irradiated by said excitation rays at time ( $t_i$ ), the sharpness of the obtained image is regardless of the diffusion of said fluorescence.

5 Some methods to improve the sharpness of the radiographic image have thus been proposed, including: a method of incorporating certain white powder into a layer containing a stimuable phosphor of a radiographic image storage panel (Japanese Patent O.P.I. Publication No. 146447/1980); and a method of coloring a radiographic image storage panel so that the mean reflecting rate of excitation rays of the stimuable phosphor is lower than the reflecting rate of rays of the stimuable fluorescent wavelength region (Japanese Patent O.P.I. Publication No. 163500/1980, for example). These methods however bring about the reduction of sensitivity inevitably in exchange of the improvement of image sharpness, and so are not considered desirable.

10 EP—A—102,790 discloses a storage panel which has a stimuable phosphor layer which is contained in a layer of powdered glass. This layer may either be spread after being mixed with butyl acetate and polyvinyl butyral or held in place between a nickel metal plate and a sheet of transparent glass.

The present invention overcomes some of the above drawbacks and contradictions in the prior art of radiographic image storage panels using stimuable phosphors, as to provide a panel having improved radiosensitivity and giving a very sharp image coupled with a lack of graininess.

20 According to the present invention there is provided a radiographic image storage panel which has at least one layer containing a laser-stimuable phosphor characterised in that the said layer is formed by sputtering or vacuum evaporation and that the said layer contains substantially no binder.

In addition, the invention relates to the use of said radiographic image storage panel for recording and reading out a radiographic image.

25 When the vacuum evaporation or sputtering technique is applied, it is possible that the stimuable phosphor penetrates into the support, undercoating or protective layer, or that the binder in the undercoating or protective layer introduces into the layer containing a stimuable phosphor. However, since the possibility of mixed layers produced by such permeation or intrusion action as above are considered as negligible from the practical viewpoint, it can be ignored.

30 As mentioned above, according to the invention, the packing density ratio and the sensitivity to X-rays of the layer containing a stimuable phosphor are improved because of the absence of binder therein. The absence of binder also causes the directivity of the layer containing a stimuable phosphor to improve, resulting in both an improvement in sensitivity through the detectability of stimuable fluorescence from the inside of the layer containing a stimuable phosphor, and an improvement in the image sharpness through the reduction of diffusion of the emitted stimuable rays.

35 Furthermore, the absence of binder in the layer containing a stimuable phosphor of the invention causes the packing density ratio of the stimuable phosphor to improve, resulting in an improvement in image graininess through the reduction of both quantum mottles by radioactive rays, and of structural mottles in the layer containing the stimuable phosphor.

### 40 Brief description of the drawings

Fig. 1 illustrates the relation between the layer thickness or the quantity adhered and the relative radiosensitivity in the radiographic image storage panel of the invention. Fig. 2(a) and (b) show samples of support used in the invention; Figs. 2(c) and (d) show samples of sectional view of said radiographic image storage panel where the layer containing a stimuable phosphor is provided onto said support. Fig. 3 illustrates the relation between the layer thickness or the quantity adhered and the relative radiosensitivity in the conventional radiographic image storage panel. Fig. 4 illustrates the relation between the layer thickness and the modulation transfer function (MTF) at 2 cycles/mm of spatial frequency in the conventional radiographic image storage panel. Fig. 5 is a schematic drawing of the radiographic image storage method used in the invention.

### 50 Detailed description of the invention

In the radiographic image storage panel of the invention, "stimuable phosphor" refers to the phosphor which, after the initial irradiation by light or high-energy radioactive rays, emits stimuable luminescence corresponding to the dose of initial irradiation which is induced by optical stimulation, (that is, stimuable excitation), and, preferably from the practical viewpoint, the phosphor is induced by excitation rays with 500 nm or longer wavelength. As a stimuable phosphor for use in the radiophotographic image storage panel of the invention, the following phosphors are for example useful:

phosphors represented by  $\text{BaSO}_4\text{:A}_x$  (where A is at least one element among Dy, Tb and Tm, and x satisfies  $0.001 \leq x < 1$  mol %) and described in Japanese Patent O.P.I. Publication No. 80487/1973;

60 phosphors represented by  $\text{MgSO}_4\text{:A}_x$  (where A is either Ho or Dy, and x satisfies  $0.001 \leq x \leq 1$  mol %), and described in Japanese Patent O.P.I. Publication No. 80488/1973;

phosphors represented by  $\text{SrSO}_4\text{:A}_x$  (where A is at least one element among Dy, Tb and Tm, and x satisfies  $0.001 \leq x < 1$  mol %); and described in Japanese Patent O.P.I. Publication No. 80489/1973;

65 phosphors composed of  $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$  or  $\text{BaSO}_4$  containing at least one element among Mn, Dy and Tb, and described in Japanese Patent O.P.I. Publication No. 29889/1976;

# EP 0 175 578 B1

phosphors composed of  $\text{BeO}$ ,  $\text{LiF}$ ,  $\text{MgSO}_4$  or  $\text{CaF}_2$ , and described in Japanese Patent O.P.I. Publication No. 30487/1977;

phosphors composed of  $\text{Li}_2\text{B}_4\text{O}_7$ :Cu or Ag, and described in Japanese Patent O.P.I. Application No. 39277/1978;

5 phosphors represented by either  $\text{Li}_2\text{O} \cdot (\text{B}_2\text{O}_3)_x\text{:Cu}$  (where  $x$  satisfies  $2 < x \leq 3$ ), or  $\text{Li}_2\text{O}(\text{B}_2\text{O}_3)_x\text{:Cu}$ , A (where  $x$  satisfies  $2 < x \leq 3$  again), and described in Japanese Patent O.P.I. Publication No. 47883/1979;

phosphors represented by  $\text{SrS:Ce}$ ,  $\text{Sm}$ ;  $\text{SrS:Eu}$ ,  $\text{Sm}$ ;  $\text{La}_2\text{O}_3\text{:S:Eu}$ ,  $\text{Sm}$ ; and  $(\text{Zn}, \text{Cd})\text{S:Mn}$ , X (where X is halogen), and described in U.S. Patent 3,859,527;

10 phosphors represented by  $\text{ZnS:Cu}$  or Pb, barium aluminate phosphors represented by  $\text{BaO} \cdot x\text{Al}_2\text{O}_3\text{:Eu}$  (where  $x$  satisfies  $0.8 \leq x \leq 10$ ) and alkali earth silicate phosphors represented by  $\text{M}''\text{O} \cdot x\text{SiO}_2\text{:A}$  (where  $\text{M}''$  is Mg, Ca, Sr, Zn, Cd or Ba; A is at least one element among Ce, Tb, Eu, Tm, Pb, Tl, Bi and Mn; and  $x$  satisfies  $0.5 \leq x < 2.5$ ) of Japanese Patent O.P.I. Publication No. 12142/1980;

alkali earth fluorohalide phosphors represented by  $(\text{Ba}_{1-x-y}\text{Mg}_x\text{Ca}_y)\text{FX:eEu}^{2+}$  (where X is at least one of Br and Cl; and  $x$ ,  $y$  and  $e$  satisfy  $0 < x + y \leq 0.6$ ,  $xy \neq 0$ , and  $10^{-8} \leq e \leq 5 \times 10^{-2}$ , respectively);

15 phosphors represented by  $\text{LnOX:xA}$  (where Ln is at least one element among La, Y, Gd and Lu; X is Cl and/or Br; A is Ce and/or Tb; and  $x$  satisfies  $0 < x < 0.1$ ), and described in Japanese Patent O.P.I. Publication No. 12144/1980;

phosphors represented by  $(\text{Ba}_{1-x}\text{M}''x)\text{FX:yA}$  (where  $\text{M}''$  is at least one element among Mg, Ca, Sr, Zn and Cd; X is at least one element among Cl, Br and I; A is at least one element among Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb and Er;  $x$  and  $y$  satisfy  $0 \leq x \leq 0.6$  and  $0 \leq y \leq 0.2$ , respectively), and described in Japanese Patent O.P.I. Publication No. 12145/1980;

20 phosphors represented by  $\text{BFX:xCe}$ , yA (where X is at least one element among Cl, Br and I; A is at least one element among In, Tl, Gd, Sm and Zr;  $x$  and  $y$  satisfy  $0 < x \leq 2 \times 10^{-1}$  and  $0 < y \leq 5 \times 10^{-2}$ , respectively), and described in Japanese Patent O.P.I. Publication No. 84389/1980; rare-earth element-activated divalent metal fluorohalide phosphors represented by  $\text{M}''\text{FX} \cdot x\text{A:yLn}$  (where  $\text{M}''$  is at least one element among Mg, Ca, Ba, Sr, Zn and Cd; A is at least one oxide among BeO, MgO, CaO, SrO, BaO, ZnO,  $\text{Al}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{GeO}_2$ ,  $\text{SnO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{ThO}_2$ ; Ln is at least one element among Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Sm and Gd; X is at least one element among Cl, Br and I;  $x$  and  $y$  satisfy  $5 \times 10^{-5} \leq x \leq 0.5$  and  $0 < y \leq 0.2$ , respectively), and described in Japanese Patent O.P.I. Publication No. 160078/1980; and

30 phosphors represented by either  $x\text{M}_3(\text{PO}_4)_2 \cdot \text{NX}_2\text{:yA}$  or  $\text{M}_3(\text{PO}_4)_2 \cdot \text{yA}$  (where each of M and N is at least one element among Mg, Ca, Sr, Ba, Zn and Cd; X is at least one element among F, Cl, Br and I; A is at least one element among Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Sb, Tl, Mn and Sn; and  $x$  and  $y$  satisfy  $0 < x \leq 6$  and  $0 \leq y \leq 1$ , respectively); phosphors represented by either  $n\text{ReX}_3 \cdot m\text{AX}'_2\text{:xEu}$  or  $n\text{ReX}_3 \cdot m\text{AX}'_2\text{:xEu}$ , ySm (where Re is at least one element among La, Gd, Y and Lu; A is at least one element among Ba, Sr and Ca; each of X and X' is at least one element among F, Cl and Br;  $x$  and  $y$  satisfy  $1 \times 10^{-4} < x < 3 \times 10^{-1}$  and  $1 \times 10^{-4} < y < 1 \times 10^{-1}$ , respectively; and  $n/m$  satisfies  $1 \times 10^{-3} < n/m < 7 \times 10^{-1}$ ); alkaline halide phosphors represented by  $\text{M}'\text{X} \cdot a\text{M}''\text{X}'_2 \cdot b\text{M}'''\text{X}''_3\text{:cA}$  (where  $\text{M}'$  is at least one alkaline metal selected from among Li, Na, K, Rb and Cs;  $\text{M}''$  is at least one divalent metal selected from among Be, Mg, Ca, Sr, Ba, Zn, Cd, Cu and Ni;  $\text{M}'''$  is at least one trivalent metal selected from among Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Al, Ga and In; each of X, X' and X'' is at least one halogen selected from among F, Cl, Br and I; A is at least one metal selected from Eu, Tb, Ce, Tm, Dy, Pr, Ho, Nd, Yb, Er, Gd, Lu, Sm, Y, Tl, Na, Ag, Cu and Mg; and the values  $a$ ,  $b$  and  $c$  satisfy  $0 \leq a < 0.5$ ,  $0 \leq b < 0.5$  and  $0 < c \leq 0.2$  respectively) of Japanese Patent O.P.I. Publication No. 148285/1982.

45 Among these types of phosphors, alkali halide phosphors are especially preferable because their easy formability of a layer containing a stimutable phosphor by means of vacuum evaporation, sputtering or the like.

However, the stimutable phosphors used in the radiographic image storage panel of the invention are not limited to above-mentioned phosphors, but include any phosphor if it can exhibit stimutable luminescence on irradiation with excitation rays after radiation by radioactive rays, provided it can be deposited by sputtering or vacuum deposition.

Said stimutable phosphor is lamellarly deposited without binder on a support by sputtering or vacuum evaporation to form a layer containing the stimutable phosphor, resulting in the formation of the radiographic image storage panel of the invention.

55 The radiographic image storage panel of the invention may also comprise two or more stimutable phosphor layers containing at least one laser stimutable phosphor. The stimutable phosphor which comprises the individual stimutable phosphor layers may be the same or different from each other.

The manufacturing methods of the radiographic image storage panels of the invention whose stimutable phosphor layers contain no binder are as follows:

60 The first method is vacuum evaporation. In this process, a vacuum evaporating apparatus in which the support has been placed is evacuated to a level of, say,  $10^{-6}$  Torr. Then, at least one laser-stimutable phosphor is vaporized by means of resistive heating, electron beam heating or the like to have a layer of said phosphor with a desired thickness formed on the surface of said support, resulting in the formation of a layer containing said stimutable phosphor without binder.

65 In this vacuum evaporating method, the said layer containing a stimutable phosphor may also be

formed by repeating the vaporizing procedure. In addition, co-vacuum evaporation using a number of resistive heaters or electron beams may be performed.

After the vacuum evaporating operation, the layer containing stimuable phosphor is provided, if necessary, with a protective layer on the side opposite to the said support, to complete the radiographic image storage panel of the invention. Alternatively, the layer containing a stimuable phosphor may be formed on a previously formed protective layer, and then provided with a support.

In this vacuum evaporating method, it is also possible to have precursors of stimuable phosphors co-vaporized using a number of resistive heaters or electron beams in order to synthesize the intended stimuable phosphor on a support, and to have the layer containing a stimuable phosphor formed concurrently.

In this vacuum evaporating method, the said support or protective layer onto which the said stimuable phosphor is to be deposited may be cooled or heated, during vaporizing if necessary, or the deposited layer may be heat-treated after vaporizing.

The second method is a sputtering technique. In this process, a sputtering apparatus in which the support has been placed is evacuated to a level of, say,  $10^{-6}$  Torr then an inert gas such as Ar or Ne is introduced into said apparatus to raise the inner pressure up to a level of, say,  $10^{-3}$  Torr. Then at least one laser stimuable phosphor is sputtered to deposit onto the surface of said support a layer of said phosphor with a desired thickness.

In this sputtering method, the layer containing a stimuable phosphor may be formed by repeating a number of sputtering procedures. A layer containing stimuable phosphor may also be formed by using, sequentially or concurrently, different stimuable phosphors.

After the sputtering operation, the layer containing a stimuable phosphor is provided, if necessary, with a protective layer on the side opposite to said support, to complete the radiographic image panel of the invention. Alternatively, the layer containing a stimuable phosphor may be formed on a protective layer first, and provided with a support.

In this sputtering method, it is also possible to employ a number of precursors of stimuable phosphors as targets, and to sputter them concurrently or in order to synthesize the intended stimuable phosphor on the support, and to have a layer containing the stimuable phosphors formed concurrently. In this sputtering method, a reactive sputtering technique may be used if necessary by introducing a gas such as  $O_2$  or  $H_2$  into the apparatus. Furthermore, the support or protective layer may be cooled or heated during sputtering if necessary. The deposited layer may be heat-treated after sputtering.

The thickness of the layer containing a stimuable phosphor of the radiographic image storage panel of the invention can be varied according to the radiosensitivity of the intended radiographic image storage panel, and the type of the stimuable phosphor, but is preferably from 30  $\mu m$  to 1000  $\mu m$ , especially from 50  $\mu m$  to 800  $\mu m$ .

When the thickness of the stimuable phosphor layer is less than 30  $\mu m$ , the radiation absorbance thereof tends to deteriorate markedly, and thereby, the radiation sensitivity is lowered and the graininess of an image therefrom is increased. In addition to the foregoing, the stimuable phosphor layer may be rendered transparent, and thereby, the two dimensional spreading of stimuable excitation rays in the stimuable phosphor layer is increased, which results in the deterioration of image sharpness.

Fig. 1 illustrates the relation between the thickness (or the corresponding quantity adhered), and the radiosensitivity of the stimuable phosphor in the radiographic image storage panel of the invention. Since the layer containing a stimuable phosphor of the radiographic image storage panel of the invention does not contain any binder, the quantity adhered of stimuable phosphor (or its packing ratio) is about 2 times that of a conventional radiographic image storage panel, as can be seen by comparing Figs. 3 and 4. Therefore, according to the invention, the improvement of the absorption rate of radiation per unit thickness of layer containing a stimuable phosphor not only produces a radiosensitivity much higher compared to the conventional radiographic image storage panel, but also causes a certain improvement of the graininess of the image.

In addition, since the layer of a stimuable phosphor of the radiographic image storage panel of the invention does not contain any binder, it has a high directivity of excitation rays and stimuable luminescence compared to conventional radiographic image storage panels, making it possible to thicken said panel.

Furthermore, since the layer containing a stimuable phosphor of the radiographic image storage panel of the invention has a good directivity, the dispersion of stimuable excitation rays in the layer containing the stimulus phosphor is reduced, resulting in a remarkable improvement of image sharpness.

As a support used in the radiographic image storage panel of the invention, various polymer materials, glass, tempered glass, metals and the like can be used. Among them, flexible or easily roll-processable sheet materials are especially suitable in view of the handling of information recording material. From this point of view, the especially preferable material of support is, for example, plastic film such as cellulose acetate, polyester, polyethylene terephthalate, polyamide, polyimide, cellulose triacetate or polycarbonate film, or metallic sheets such as aluminum, steel or copper sheet.

The surface of such a support may not only be flat but also matt for the purpose of improving its adhesiveness to the layer containing a stimuable phosphor. Matting can be achieved by, for example, a method for making a rugged surface as shown in Fig. 2(a) or a method for making a structure with

## EP 0 175 578 B1

separately spread small tile-like plates as shown in Fig. 2(b), in addition to a method wherein a matting agent is used. Such an uneven surface as shown in Fig. 2(a) further improves the image sharpness, because the layer containing a stimutable phosphor thereon is finely divided by its unevenness as shown in Fig. 2(c). Such an irregular surface as shown in Fig. 2(b) also further improves the image sharpness, because the layer containing a stimutable phosphor is deposited thereon retaining substantially the irregularity of the surface of the support, and because, consequently, the layer containing a stimutable phosphor is composed of a number of small pile-like blocks separated from each another by cracks as shown in Fig. 2(d).

In addition, the support used in the invention may first be provided with an undercoat layer on its interface with the layer containing a stimutable phosphor for the purpose of improving its adhesiveness to said layer. The thickness of the support can be selected according to the nature of its material, but generally ranges from 100  $\mu\text{m}$  to 1500  $\mu\text{m}$ , and preferably from 100  $\mu\text{m}$  to 1000  $\mu\text{m}$  for ease of handling.

In the radiographic image storage panel of the invention, the layer containing a stimutable phosphor may be provided with a protective layer on the side opposite to said support for the purpose of protecting said layer containing a stimutable phosphor physically or chemically. Such a protected layer can be provided by coating a liquid composition directly on said layer containing a stimutable phosphor, or by making the layer separately and sticking it thereto. As the material for the protective layer, there can be used usual protective material such as cellulose acetate, nitrocellulose, polymethyl methacrylate, polyvinyl butyral, polyvinyl formal, polycarbonate, polyester, polyethylene terephthalate, polyethylene, polyvinylidene chloride and nylon. Usually the thickness of the protective layer is 1  $\mu\text{m}$  to 40  $\mu\text{m}$ .

The radiographic image storage panel of the invention provides very good sharpness, graininess and sensitivity when used by the radiographic image storage method diagrammatically illustrated in Fig. 5. In Fig. 5, 51 is a radiation generating device; 52 is a subject; 53 is a radiographic image storage panel of the invention; 54 is a source of stimutable excitation rays; 55 is a photoelectric conversion device which detects the stimutable fluorescence emitted from said panel 53; 56 is a device which regenerates detected signals as an image; 57 is a displaying device which displays said regenerated image; and 58 is a screen which separates stimutable fluorescence from stimutable excitation rays, and transmits the only stimutable fluorescence. 53 to 55 are not limited to the above description so long as they serve to regenerate the optical information in any form.

As shown in Fig. 5, radioactive rays generated by the radiation generating device 51 are transmitted by the subject 52, and pass into the radiographic image storage panel 53. These radioactive rays are absorbed by the layer containing a stimutable phosphor of said panel 53, and their energy is accumulated therein, resulting in the formation of an accumulative image of radiation transmission. Subsequently, the stimutable fluorescence is emitted by exciting this accumulative image by excitation rays from the source 54. Since the layer containing a stimutable phosphor does not contain binder, and so has highly directivity, any diffusion of the excitation rays in the layer containing a stimutable phosphor on scanning said layer with said rays is suppressed.

Since the intensity of the emitted stimutable fluorescence is proportional to the quantity of the accumulated radiation energy, the radiation transmission image of the subject 52 can be observed by photoelectrically converting the optical signals using the device 55 such as a photomultiplying tube, and by regenerating as an image using the device 56 and displaying using the device 57.

The invention is further described with reference to the following Examples.

### Example 1

First, a 300  $\mu\text{m}$ -thick black polyethylene terephthalate film as a support is placed in a vacuum evaporating apparatus. Alkali halide stimutable phosphor ( $0.9 \text{ RbBr} \cdot 0.1 \text{ CsF} : 0.01 \text{ Ti}$ ) is placed in a tungsten boat for resistive heating, which is then wired to a couple of electrodes for resistive heating. Subsequently, the vacuum evaporating apparatus is evacuated to  $2 \times 10^{-6}$  Torr.

Next, by charging the tungsten boat with electricity, the alkali halide stimutable phosphor is vaporized until the thickness of the stimutable phosphor layer formed on the polyethylene terephthalate film reaches 300  $\mu\text{m}$  to obtain radiographic image storage panel A of the invention.

The radiographic image storage panel A is irradiated by 10m R of X-rays from a lamp voltage of 80 KVp, and subsequently stimably excited by a He-Ne laser beam of 633 nm. The stimutable fluorescence emitted by the layer containing the stimutable phosphor is photoelectrically converted by a light detector (i.e. a photomultiplying tube), and the signals obtained are regenerated as an image using an image regenerator, and recorded on a silver salt film. The sensitivity of the radiographic image storage panel A to X-rays is measured by examining the size of signal, and the modulation transfer function (MTF) and the graininess of the obtained image. The results are shown in Table 1.

In Table 1, the sensitivity to X-rays is represented by a relative index with 100 as the sensitivity of panel A. The MTF is the value at a spatial frequency of 2 cycles per mm. The graininess is evaluated as good, moderate and poor.

### Example 2

Procedures of Example 1 are repeated, except for, instead of 300  $\mu\text{m}$ , the said layer has a thickness of 150  $\mu\text{m}$ , to obtain the radiographic image storage panel B of the invention.

## EP 0 175 578 B1

The radiographic image storage panel B is evaluated in the same way as in Example 1. The results are shown in Table 1.

### Example 3

Procedures of Example 1 are repeated, except, instead of the film of Example 1 as a support, a black polyethylene terephthalate film whose surface is provided with a jagged pattern is used, to obtain the radiographic image storage panel C of the invention.

The jagged pattern comprises a grid of 10  $\mu\text{m}$ -wide and 100 $\mu\text{m}$ -high projecting parts, alternating between 100  $\mu\text{m}$ -by-100  $\mu\text{m}$  depressed parts.

The obtained radiographic image storage panel C is evaluated in the same way as in Example 1. The results are shown in Table 1.

### Example 4

Procedures of Example 1 are repeated to obtain the radiographic image storage panel D of the invention. However, a separated tile-pattern structure is used instead of the film of Example 1 as support. This structure is made by first treating the surface of a 0.5 mm-thick aluminum sheet with anode oxidation, and treating the sheet to seal holes. Then the aluminum sheet is heat-treated over 200°C to generate a number of cracks throughout the aluminum oxide layer. Thus a structure having a number of tile-like small chips separated one another by said cracks throughout its surface is obtained as a support.

The obtained radiographic image storage panel D is evaluated in the same way as in Example 1. The results are shown in Table 1.

### Control 1

Eight (8) wt. parts of alkaline halide stimuable phosphor (0.9 RbBr · 0.1 CsF:0.01 Ti) and 1 wt. part of polyvinyl butyral resin are added to and dispersed into 5 wt. parts of cyclohexanone. This dispersion is evenly applied onto a 300  $\mu\text{m}$ -thick black polyethylene terephthalate film horizontally held as a support, and air-dried to form a 300  $\mu\text{m}$ -thick layer containing the stimuable phosphor.

The radiographic image storage panel obtained (control P) is evaluated in the same way as in Example 1. The results are shown in Table 1.

### Control 2

Procedures of Control 2 are repeated, except instead of 300  $\mu\text{m}$ , the thickness of the layer containing the stimuable phosphor is 150  $\mu\text{m}$ .

The radiographic image storage panel obtained (control Q) is evaluated in the same way as in Example 1. The results are shown in Table 1.

TABLE 1

Panel	Layer thick, $\mu\text{m}$	Sensitivity to X-rays	Graininess	Sharpness, %
(Example)				
A	300	100	good	37
B	150	51	moderate	45
C	300	94	good	45
D	300	95	good	47
(Control)				
P	300	50	moderate	30
Q	150	24	poor	40

As seen in Table 1, the radiographic image storage panels A to D have roughly twice the sensitivity to X-rays, and have better image graininess compared to the respective Controls P and Q being the same in thickness of the layer containing a stimuable phosphor. The results obtained are because the layer containing a stimuable phosphor of the radiographic image storage panel of the invention has a higher packing ratio and a better absorption rate of X-rays compared to that of the control panel due to the absence of binder in the former layer.

In addition, although the radiographic image storage panels A to D are higher in sensitivity to X-rays as above, the image sharpness compared to Control P and Q, respectively. These results are on account of the reduced dispersing of the stimably exciting He-Ne laser beam in the layer containing a stimuable phosphor of the radiographic image storage panel of the invention because of the high directivity of said layer due to the absence of binder thereon.

The supports of radiographic image storage panels C and D of the invention are particularly useful. The layer containing a stimuable phosphor of panel C is finely divided into minute projecting and depressed parts; the layer of panel D is finely divided by the effect of a number of fine cracks provided on the surface

## EP 0 175 578 B1

of its support. Consequently, it becomes possible to further reduce dispersing of the excitation rays in the layer containing a stimuable phosphor, resulting in the further improvement of the image sharpness.

### Example 5

- 5 As a support, 300  $\mu\text{m}$ -thick black polyethylene terephthalate film is placed in a sputtering apparatus. Then as a target of sputtering, alkaline halide stimuable phosphor ( $0.95 \text{ RbBr} \cdot 0.05 \text{ CsF} : 0.005 \text{ TI}$ ) is placed in the sputtering apparatus, and subsequently the apparatus is evacuated to  $1 \times 10^{-6}$  Torr. Sputtering is conducted while introducing Ar gas as a sputter gas, until the thickness of the layer containing the stimuable phosphor depositing on said polyethylene terephthalate film reaches 300  $\mu\text{m}$  to obtain the
- 10 radiographic image storage panel E of the invention.

The obtained panel E is evaluated in the same way as in Example 1. The results are shown in Table 2.

TABLE 2

15	Panel	Layer thick, $\mu\text{m}$	Sensitivity to X-rays	Graininess	Sharpness, %
	E	300	100	good	36

- 20 As seen in Table 2, the radiographic image storage panel E produced by sputtering exhibits good sensitivity to X-rays, graininess as well as sharpness, similar to panels A to D.

### Claims

- 25 1. A radiographic image storage panel which has at least one layer containing a laser-stimulable phosphor characterised in that the said layer is formed by sputtering or vacuum evaporation and that the said layer contains substantially no binder.
2. A radiographic image storage panel according to claim 1, wherein the total thickness of said layer containing a stimuable phosphor is from 30  $\mu\text{m}$  to 1000  $\mu\text{m}$ .
- 30 3. A radiographic image storage panel according to claim 1 or 2, wherein the support of said panel has a matt surface.
4. A radiographic image storage panel according to any one of claims 1 to 3, wherein said stimuable phosphor is an alkali halide phosphor.
5. Use of a radiographic image panel as defined in claim 1 for recording and reading out a radiographic
- 35 image, wherein:
- (a) radiation energy corresponding to a radiographic image is stored in the laser-stimulable phosphor layer of said panel,
- (b) said layer is scanned with a laser to release said stored energy as fluorescence, and
- (c) said fluorescence is detected to form an image.
- 40 6. Use according to claim 5, wherein the total thickness of said layer is 30  $\mu\text{m}$  to 1000  $\mu\text{m}$ .
7. Use according to claim 5, wherein said panel has a support which has a matt surface.
8. Use according to claim 5, wherein said laser-stimulable phosphor is an alkali halide phosphor.

### Patentansprüche

- 45 1. Röntgenbildspeicherplatte mit mindestens einer Schicht mit einem laserstimulierbaren Leuchtstoff, dadurch gekennzeichnet, daß die betreffende Schicht durch Zerstäubung oder Vakuumbedampfung gebildet ist und praktisch in Bindemittel enthält.
2. Röntgenbildspeicherplatte nach Anspruch 1, dadurch gekennzeichnet, daß die Gesamtdicke der
- 50 Schicht mit einem stimulierbaren Leuchtstoff 30  $\mu\text{m}$  bis 1000  $\mu\text{m}$  beträgt.
3. Röntgenbildspeicherplatte nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß ihr Schichtträger eine matte Oberfläche aufweist.
4. Röntgenbildspeicherplatte nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß der stimulierbare Leuchtstoff aus einem Alkalihalogenid-Leuchtstoff besteht.
- 55 5. Verwendung einer Röntgenbildplatte nach Anspruch 1 zum Aufzeichnen und Ablesen eines Röntgenbildes.



## EP 0 175 578 B1

8. Verwendung nach Anspruch 5, dadurch gekennzeichnet, daß der laserstimulierbare Leuchtstoff aus einem Alkalihalogenidleuchtstoff besteht.

### Revendications

5

1. Panneau de stockage d'image radiographique, qui présente au moins une couche contenant un phosphore stimuable par laser, caractérisé en ce que ladite couche est formée par pulvérisation ou évaporation sous vide, et en ce que ladite couche ne contient pratiquement pas de liant.

10 2. Panneau de stockage d'image radiographique, selon la revendication 1, dans lequel l'épaisseur totale de ladite couche contenant un phosphore stimuable est de 30 µm à 1000 µm.

3. Panneau de stockage d'image radiographique, selon la revendication 1 ou 2, dans lequel le support dudit panneau présente une surface mate.

4. Panneau de stockage d'image radiographique, selon l'une quelconque des revendications 1 à 3, dans lequel ledit phosphore stimuable est un phosphore d'halogénure alcalin.

15 5. Utilisation d'un panneau de stockage d'image radiographique, tel que défini à la revendication 1, pour l'enregistrement et la lecture d'une image radiographique, dans laquelle:

(a) l'énergie rayonnante correspondant à une image radiographique est stockée dans la couche de phosphore stimuable par laser dudit panneau,

20 (b) ladite couche est balayée par un laser pour libérer ladite énergie stockée sous forme de fluorescence, et

(c) ladite fluorescence est détectée pour former une image.

6. Utilisation selon la revendication 5, dans lequel l'épaisseur totale de ladite couche est de 30 µm à 1000 µm.

25 7. Utilisation selon la revendication 5, dans laquelle ledit panneau présente un support qui a une surface mate.

8. Utilisation selon la revendication 5, dans laquelle ledit phosphore stimuable par laser est un phosphore d'halogénure alcalin.

30

35

40

45

50

55

60

65

FIG. 1

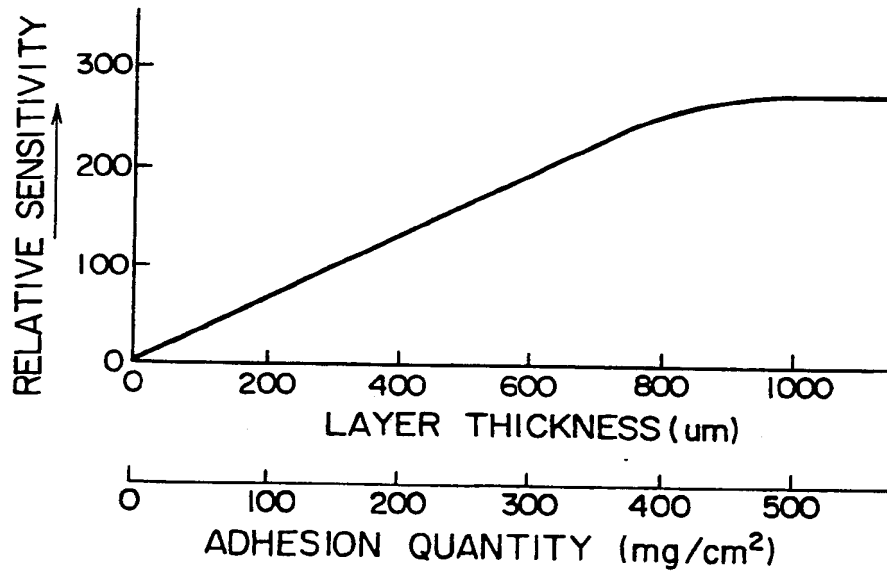


FIG. 2

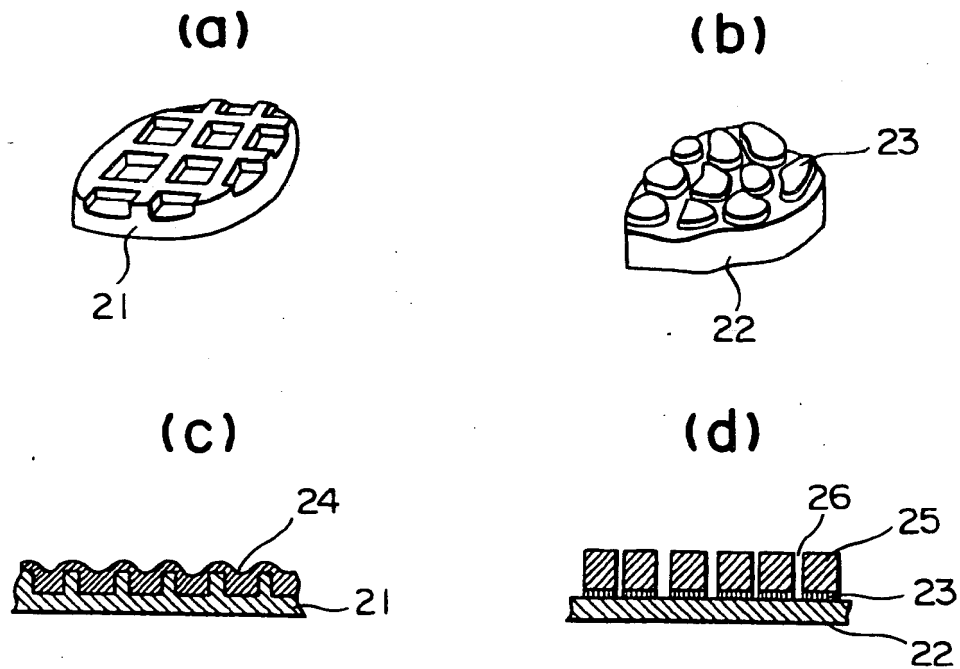


FIG. 3

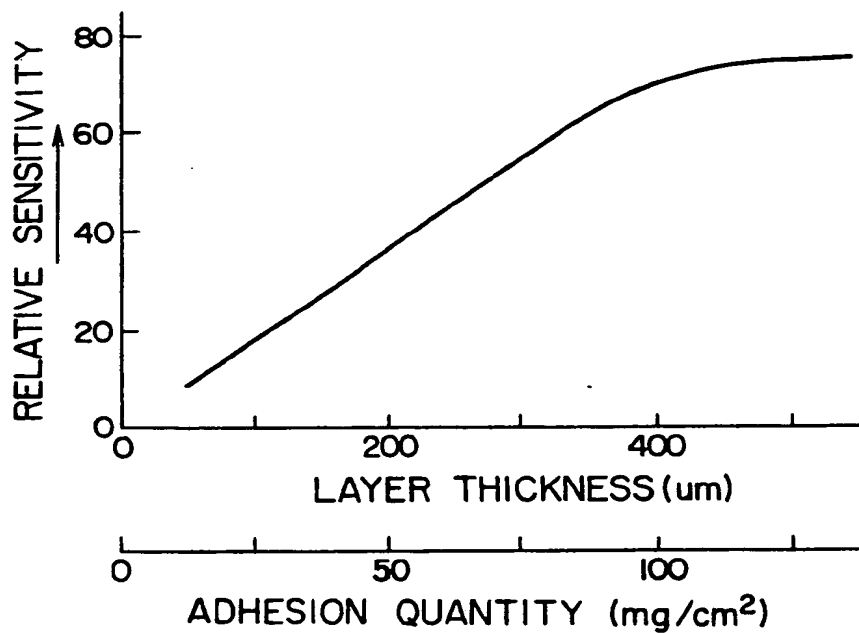


FIG. 4

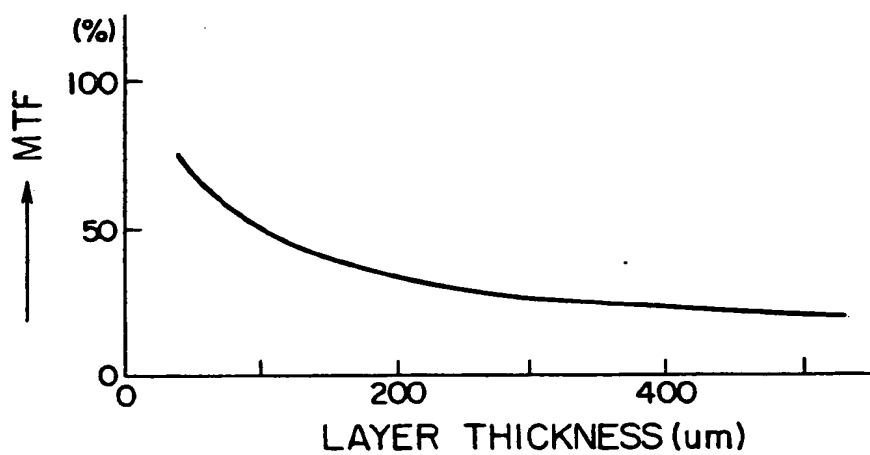


FIG. 5

